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(54) FUEL CELL CATALYST ELECTRODE

(71) We, UNITED AIRCRAFT CORPORATION, a Corporation organized and existing under the laws of the State of Delaware, United States of America, of 400 Main Street, East Hartford, Connecticut, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to a novel catalyst suitable for use as an electrode in typical fuel cells, such as hydrogen-oxygen or hydrogen-air fuel cells. More particularly, it relates to a novel catalytic electrode comprising an alloy of platinum and nickel having a coating of tungsten oxide. The catalyst can be used in fuel cells which employ a hydrogen fuel that can be contaminated with carbon monoxide.

A fuel cell is a device which converts the energy of a chemical reaction between a fuel and oxidant directly into low voltage, direct current electricity. In obtaining an efficient fuel cell, the problems encountered are essentially problems of chemical kinetics. It is necessary that the reaction between the fuel and oxidant occurs in such manner that the amount of energy degraded into heat is as small as possible. At the same time, the reaction rate of the cell must be high enough to produce economically sufficient current from a cell of practical size.

A typical fuel cell comprises a fuel electrode or anode, an oxidant electrode or cathode, an electrolyte positioned between the electrodes and means to introduce fuel and oxidant to their respective electrodes. In operation, air or oxygen is forced through the cathode where the oxidant reacts at a catalytic surface with the electrolyte within the pores of the electrode. Hydroxyl ions and either free oxygen or water are formed, with the hydroxyl ions passing through the pores of the electrode into the electrolyte for transference to the anode. At the anode, fuel enters and impinges on the electrode where a process of adsorption, reaction and desorption occurs. In an acid system, the fuel molecules are dissociated, oxidized and the positive part of the molecule migrates to the cathode where it combines with the negative moiety of the oxidant, forming a neutral product. The electrical charges are drawn from the electrode or a closely spaced current collector to an external circuit.

Fuel cells are particularly attractive commercially due to their potential performance characteristics. Cells having an efficiency of up to about 90% have been constructed, which is far superior to the efficiency of a gas turbine, which has a theoretical maximum efficiency of only about 30% as set forth in Carnot's Heat Law. Since a fuel cell is not governed by heat considerations, the theoretical efficiencies are not so limited.

In an effort to obtain a fuel cell which is practical on a commercial scale, a great deal of research has been carried out in an effort to find improved electrodes. Thus, in the prior art, fuel cell electrodes have been constructed of nickel, and other electrodes suggested of platinum or rhodium. Such electrodes have been found to possess many desirable characteristics in a fuel cell. It has now been found that outstanding characteristics are obtained when alloys of platinum and nickel, sometimes with rhodium, together, together with a precipitated coating of tungsten oxide are employed as fuel cell electrodes. Such electrodes, while providing excellent electrochemical performance characteristics, are substantially unaffected by the corrosive influences of a fuel cell and have an extremely high surface area which extends the catalyst over large surface areas.

Fuel gases other than purified hydrogen have been used with fuel cells. One of the more common is the product obtained by passing steam-reformed natural gas (RNG) through a shift converter. The gas is composed mainly of hydrogen and carbon dioxide, but also contains a small concentration of carbon monoxide. When this gas is used at the anode of an acid fuel cell in which

platinum is the catalyst, the carbon monoxide rapidly poisons the platinum, thereby seriously reducing the performance level of the electrode. Ideally, a catalyst for use in an acid fuel cell using reformed gas must have a tolerance for carbon monoxide, a hydrogen activity equivalent to platinum black and be capable of long time operation using the smallest weight possible. Poisoning of the platinum by carbon monoxide becomes less noticeable as the temperature is raised. But the use of elevated temperatures raises the rate of corrosion and markedly reduces the life of the cell. Methods are available to remove carbon monoxide from RNG, by methanation or preferred oxidation, for example, but these adaptations increase both the cost and complexity of the system.

An anode catalyst which will operate efficiently at 120°—135°C. on unpurified RNG offers considerable advantages. The choice of this particular temperature range permits the use of waste heat from the cell to raise steam for the re-forming process while still maintaining corrosion at an acceptably low level. The present invention involves an anode catalyst which exhibits good tolerance to carbon monoxide and resistance to corrosion in 85% phosphoric acid.

Binary alloys of platinum and nickel (and ternary alloys with rhodium) are known to be quite resistant to carbon monoxide poisoning. Some of these alloys also have tungsten oxide incorporated in them as a homogeneous ingredient thereof. In an article by McKee and Pak, J. Electrochemical Society: Electrochemical Technology, Vol. 116, No. 4, April 1969, pages 516—520, an alloy composition of nickel and copper with platinum is disclosed. In the United States patent to Ziering, 3,357,863, a polycomponent catalyst mixture of rhodium, platinum and tungsten oxide is disclosed.

According to the present invention an electrode for a fuel cell comprises an electrically conductive substrate and a catalyst coating disposed upon said substrate, said catalyst coating comprising an alloy of platinum with nickel, copper, iron or cobalt, the alloy being in particulate form and an adherent layer of tungsten oxide disposed upon the external surfaces of said alloy particles. Due to the techniques of preparation, substantially all of the oxides of nickel, copper, iron or cobalt plus platinum and rhodium, if present, from which the catalyst is derived, are converted into the metal. Some minor or trace amounts of the oxides, however, may not be converted and will remain within the alloy as free oxides, probably due to incomplete initial mixing during preparation.

The catalyst used according to the present invention preferably includes from 0.5 to 50 per cent by weight of the alloy and from 1 to 50 per cent by weight of the adherent layer of tungsten oxide disposed on the external surfaces of the alloy particles. The coated alloy catalyst is quite finely divided and at least about 75% of the particles are under 20 μ.

In the catalyst which we have described above, the rhodium can be added to increase the surface area. In the following Table I, various weights of rhodium are added to a nickel, platinum, rhodium:tungsten oxide catalyst. As shown, as the amount of rhodium is increased, the surface area is increased. It is to be remembered, however, that rhodium is quite expensive and its quantity should be kept to a minimum consistent with the desired surface area. Although good performance has been obtained with as little as 1 w/o rhodium, based on the weight of catalyst, the optimum amount seems to fall between 20 and 35 w/o rhodium based on the weight of catalyst.

TABLE I

Rhodium w/o of the Catalyst	Surface Area m^2/g
5	167
10	190
15	230
20	255
25	285
30	315
35	340

The alloy also contains, in addition to platinum and rhodium, substantial quantities of nickel or perhaps copper iron or cobalt. The nickel reduces the quantity of catalyst which has to be placed upon the electrode in order to achieve a desired rate of reaction. In other words, the nickel adds bulk to the catalyst and can help reduce the quantities of rhodium and platinum, thereby lowering the cost. Because of the increase in bulk, fuel cell electrodes of low loadings (1—4 g/cm^2) are easily made, while in the absence of nickel, loadings as low as 4 g/cm^2 are attained only with difficulty. To provide these benefits, as well as to increase the tolerance of the catalyst to carbon monoxide as described below, nickel can be included in quantities of from 0.5 to 50 per cent by weight of the alloy. Table II shows that the addition of nickel increases the tolerance of the catalyst to carbon monoxide poisoning.

TABLE II

Weight % of the catalyst (Weight % of the alloy) Ni	Pt	Rh	WO_3	Millivolts at 500 milliamperes (E*)
0	40	40	20	60
10 (12.50)	35 (43.75)	35 (43.75)	20	58
25 (31.25)	50 (62.50)	5 (6.25)	20	128
39 (48.75)	40 (50)	1 (1.25)	20	200

In preparing the catalysts, predetermined quantities of chloroplatinic acid, rhodium trichloride and nickel nitrate are individually dissolved in water. The quantities used are those which are the equivalent of the desired weights in the alloys and within the ranges stated. Other water soluble salts of the metals, such as their chlorides, can be used. The solutions are then mixed and poured over sodium nitrate which is preferably in great excess and generally greater than ten times the combined weight of the platinum and rhodium salts. The excess water is evaporated in an oven at 110°C. and a dry cake is produced. The cake is then broken up and the mixture is transferred to a furnace to be heated for four hours at 400°C. The cake becomes molten at these temperatures and fuses into a glassy-like melt which is then crushed and leached in a large volume of water. In the fusion, the various salts are converted into the oxides, that is platinum oxide, rhodium oxide and nickel oxide. These oxides are insoluble in water while sodium chloride which is produced dissolves and the leaching step removes it from the mixture.

A predetermined amount of sodium tungstate is dissolved in water and the solution is thoroughly mixed with the slurry of metal oxides. A large excess of a mineral acid, usually HNO_3, is mixed with the slurry and a precipitate of tungsten oxide immediately forms together with soluble sodium nitrate. The tungsten oxide precipitates upon the slurried metal oxides as an adherent coating. After standing for two hours, the acidified slurry is diluted to a large volume and the solids are left to settle out. The liquid is decanted and the solids are washed until they are free of acid.

The coated particulate oxides are then mixed in a conventional aqueous dispersion of polytetrafluoroethylene which binds the particles to each other and also binds the particles to a conductive carbon paper substrate to form an electrode. The oxide-catalyst is electrochemically reduced in acid, as is conventional, to form particles of an alloy of platinum with nickel, and rhodium, with a coating of tungsten oxide disposed on the outer surfaces of the particles. As has been noted, the reduction of the coated, particulate oxides of platinum, rhodium and nickel to the metal is substantially complete although some minor or trace amounts of the oxide may remain unreduced.

A catalyst (Pt:Rh:Ni:WO_3::35:35:10:20) was successfully tested in an 85 w/o H_3PO_4 cell at 135°C. with an average catalyst loading or weight of 3.6 g/cm² metal (viz. Ni, Pt and Rh) and a 10 w/o of the catalyst in a "Teflon" (Registered Trade Mark) binder. A fuel of hydrogen and another of hydrogen plus 1.6% CO was used. In another test, the catalyst mentioned above was used on both the anode and the cathode. The cell was run to 2500 hours and no substantial decay was seen in the anode where 3.9 g/cm² noble metal was located. At the cathode, which had a loading of 4.7 g/cm², a decay of only 0.03 mV/hour.

As ways to prepare the catalysts according to this invention, the following Examples are offered.

Example I

The following salts were each dissolved in the smallest possible quantity of water:

17.50 g $H_2PtCl_6 \cdot xH_2O$ (40 w/o Pt) = 7.00 g Pt

17.50 g $RhCl_3 \cdot xH_2O$ (40 w/o Rh) = 7.00 g Rh

10.00 g $Ni(NO_3)_2 \cdot 6H_2O$ (20 w/o Ni) = 2.00 g Ni

These solutions were then mixed together and poured over 500 g of $NaNO_3$. The mixture was heated in a crucible at 110°C. for a sufficient time to remove the water, and then the cake was broken up, transferred to a furnace and heated to 400°C. for four hours. The melt was cooled, poured into a large volume of water and washed several times to form a slurry of oxides. At that time 5.70 g of $Na_2WO_4 \cdot 2H_2O$ (equivalent of 4 g WO_3 was dissolved in a minimal amount of water and the solution was poured into the slurry of oxides. About 150 ml. of nitric acid, more than enough to precipitate all of the sodium tungsten as WO_3, was poured into the slurry.

The resulting catalyst comprised 35% (by weight) Pt, 35% (by weight) Rh and 10% (by weight) Ni in the form of alloy particles coated with 20% (by weight) WO_3.

Example II

The following salts were each dissolved in the smallest possible quantity of water:

5.625 g $H_2PtCl_6 \cdot xH_2O$ (40 w/o Pt) = 2.25 g Pt
1.250 g $Rh\ Cl_3 \cdot xH_2O$ (40 w/o Rh) = 0.50 g Rh
3.360 g $Cu\ Cl_2 \cdot 2H_2O$ (37 w/o Cu) = 1.25 g Cu

The solutions were mixed together and poured over 150 g of $NaNO_3$. The balance of the treatment was the same as described in Example I.

The resulting catalyst comprised 45% (by weight) Pt, 10% (by weight) Rh, and 25% (by weight) Cu in the form of alloy particles coated with 20% (by weight) WO_3.

Example III

The following salts were each dissolved in the smallest possible quantity of water:

18.75 g $H_2PtCl_6 \cdot xH_2O$ (40 w/o Pt) = 7.50 g Pt
1.875 g $Rh\ Cl_3 \cdot xH_2O$ (40 w/o Rh) = 0.75 g Rh
18.75 g $Ni(NO_3)_2 \cdot 2H_2O$ (20 w/o Ni) = 3.75 g Ni

The solutions were mixed together and poured over 450 g of $NaNO_3$. The balance of the treatment was the same as described in Example I.

The resulting catalyst comprised 50% (by weight) Pt, 5% (by weight) Rh and 25% (by weight) Ni in the form of alloy particles coated with 20% (by weight) WO_3.

Example IV

The following salts were each dissolved in the smallest possible quantity of water:

12.50 g $H_2PtCl_6 \cdot xH_2O$ (40 w/o Pt) = 5.00 g Pt
12.50 g $Rh\ Cl_3 \cdot xH_2O$ (40 w/o Rh) = 5.00 g Rh
8.50 g $Ni(NO_3)_2 \cdot 6H_2O$ (20 w/o Ni) = 1.70 g Ni

The solutions were mixed together and poured over 400 g of $NaNO_3$. The balance of the treatment was the same as described in Example I.

The resulting catalyst comprised 25% by weight Pt, 25% by weight Rh and 8.5% by weight Ni; in the form of alloy particles coated with 41.5% by weight WO_3.

Example V

The following salts were each dissolved in the smallest possible quantity of water:

5.00 g $H_2PtCl_6 \cdot xH_2O$ (40 w/o Pt) = 2.00 g Pt
0.25 g $Rh\ Cl_3 \cdot xH_2O$ (40 w/o Rh) = 0.10 g Rh
9.50 g $Ni(NO_3)_2 \cdot 6H_2O$ (20 w/o Ni) = 1.90 g Ni

The solutions were mixed together and poured over 175 g $NaNO_3$. The balance of the treatment was the same as described in Example I.

The resulting catalyst comprised 40% by weight Pt, 2% by weight Rh and 38% by weight Ni; in the form of alloy particles coated with 20% by weight WO_3.

It is apparent that modifications and changes can be made within the scope of the present invention which is defined by the appended claims.

WHAT WE CLAIM IS:—

1. An electrode for a fuel cell comprising an electrically conductive substrate and a catalyst coating disposed upon said substrate, said catalyst coating comprising an alloy of platinum with nickel, copper, iron or cobalt, the alloy being in particulate form and an adherent layer of tungsten oxide disposed upon the external surfaces of said alloy particles.
2. An electrode according to Claim 1, in which between 0.5 and 50% by weight of the catalyst is the alloy and between 1 and 50% by weight is the tungsten oxide.
3. An electrode according to Claim 1 or 2, in which the majority of the coated alloy particles are less than 20 microns in size.
4. An electrode according to any of Claims 1 to 3, in which the alloy contains between 0.5 and 50% by weight of copper or nickel.
5. An electrode according to any of Claims 1 to 3, in which the alloy also includes rhodium.
6. An electrode according to Claim 5, in which the alloy contains between 0.5 and 50% by weight of copper or nickel the balance being platinum and rhodium.
7. An electrode according to Claim 5 in which the alloy contains between 1 and 40% by weight of rhodium.
8. An electrode for fuel cells substantially as hereinbefore described.

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